Indian J. Phys. **51B**, 42-49 (1977)

Microwave absorption and relaxation processes in some halogenated esters in the liquid state.

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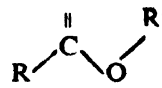
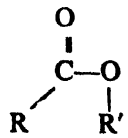
In order to study the possibility of internal rotation and ascertain molecular configurations in halogenated esters, complex dielectric permittivities have been measured at different frequencies and at different temperatures in the esters of ethyl 3-chloropropionate, methyl 3 bromopropionate and methyl-4 chlorobutyrate in the liquid state. The dielectric data were analysed in terms of two relaxation processes. The larger relaxation time τ_1 was attributed to molecular reorientation and the shorter one τ_2 to the rotation of CH_2X (X = halogen) group. The potential barriers to molecular orientation $\Delta H\tau_1$ and to internal rotatoin $\Delta H\tau_2$ have been determined. The molecular reorientation ($c_1 = 7$) was found to be the major relaxation process in all the esters. The observed values of the dipole moment was about 2.2–2.3 D and was almost temperature independent. From a comparison of the observed dipole moment and the moments estimated from bond moments and bond angles for possible conformers, the conformers present in the esters have been indicated.

1. Introduction

The general predominance of the trans conformer  over the cis conformer  in aliphatic esters such as formates and acetates has been attributed to the rigid coupling of alkyl radical of the ester group with carbonyl oxygen (Kaprovich 1954, Nozdrev 1965, Piercy and Subrahmanyan 1965, Oki and Nakanishi 1970). As a result the alkoxy group is not free to rotate about the C-O bond in formates and acetates. Dielectric relaxation

studies in these esters (Rajyam and Murty 1973) have shown that molecular reorientation is the only relaxation mechanism in these esters. In substituted esters however, though the basic ester skeleton of the compounds retains the cis configuration, the internal rotation about the C-C bond is possible and such rotation has been reported in methyl chloroacetate (Mizushima 1954), ethyl bromoacetate, halc-butyrates (Srivastava and Dinanath 1974) etc. In order to study the possibility of internal rotation and acertain the molecular configurations in some halogenated esters, dielectric absorption measurements at different microwave frequencies, have been carried out in ethyl 3 chloro-propionate, methyl 3 bromo-propionate and methyl 4-chlorobutyrate in the liquid state at different temperatures. The results of the investigations are reported and discussed in this paper.

2. Experimental

Pure samples of ethyl 3 chloropropionate, methyl 3 bromo propionate procured from Fluka (Switzerland) were distilled under reduced pressure before use in the investigations.

Apparatus : The apparatus for the dielectric measurements at microwave frequencies and static frequency were the same as described in an earlier paper (Das et al, 1973). The refractive index was measured with and Abbe refractometer, the density with a Pycnometer and the viscosity with a viscometer. Thermostat was used for maintaining the temperature of the experiment constant within $\pm$ 1°C. Estimated errors in the determination of ε' and ε'' are about 2% ad 4% respectively.

3. Results

The experimental values of ε' and ε'' are given in table 1. Cole—Cole plots (Fig 1) of the dielectric data showed high value of distribution α in all the cases indicating more than one relaxation processes in each case. The method of analysis of the data in termes of two relaxation processes was described earlier (Roy *et al*, 1976). The Calculated values of ε' and ε'' are included in Table 1 for comparison. The values of ε_0, n^2_D, ε_∞, d and η are given in table 2. The barriers to molecular orientation and internal rotation were obtained from the plots of log $\tau_1 T$ vs $\frac{1}{T}$ and log $\tau_2 T$ vs $\frac{1}{T}$ respectively. The activation energy for viscous flow was obtained from the graph log η vs $\frac{1}{T}$. The dipole moment was calculted from ε_0 and density, by using Onsager's equation. The values of τ_1, τ_2, c_1, $\Delta H\tau_1$, $\Delta H\tau_2$, $\Delta H\eta$ and μ are given in table 3.

Table 1. Observed and calculated values of dielectric permittivity ε' and dielectric loss ε''

	f = 8.59 GHz				f = 18.43 GHz				f = 23.96 GHz				f = 35.12 GHz			
T°C	ε'_{obs}	ε'_{Cal}	ε''_{obs}	ε''_{Cal}	ε'_{obs}	ε'_{Cal}	ε''_{obs}	ε''_{Cal}	ε'_{obs}	ε'_{Cal}	ε''_{obs}	ε''_{Cal}	ε'_{obs}	ε'_{Cal}	ε''_{obs}	ε''_{Cal}
							Ethyl 3 chloropropionate.									
30	5.84	5.83	2.82	2.81	4.54	4.53	2.24	2.24	4.16	4.15	2.08	2.07	3.60	3.63	1.77	1.79
50	6.00	5.99	2.85	2.85	4.47	4.46	2.29	2.29	4.08	4.09	2.08	2.08	3.59	3.59	1.78	1.77
70	6.08	6.09	2.48	2.47	4.64	4.64	2.09	2.08	4.29	4.29	1.91	1.91	3.86	3.84	1.68	1.67
							methyl 3 bromopropionate.									
30	5.80	5.60	2.78	2.80	4.20	4.37	2.15	2.21	3.96	3.99	1.98	2.01	3.48	3.49	1.64	1.66
50	5.92	5.71	2.60	2.67	4.45	4.57	2.18	2.16	4.20	4.13	2.02	2.00	3.40	3.61	1.51	1.70
70	6.10	5.68	2.40	2.48	4.58	4.55	2.04	2.06	4.15	4.19	1.98	1.97	3.30	3.68	1.42	1.76
							methyl 4 chlorobutyrate.									
30	6.55	6.11	2.21	2.38	4.85	5.00	1.95	1.94	4.59	4.70	1.80	1.84	4.05	4.23	1.58	1.69
50	6.65	6.10	2.00	2.32	4.80	4.98	1.89	1.89	4.54	4.70	1.80	1.79	4.08	4.29	1.60	1.70
70	6.72	6.33	1.72	2.08	5.25	5.20	1.92	1.85	4.74	4.91	1.80	1.77	4.20	4.50	1.60	1.72

Table 2. Values of ε_0, n^2_D, ε_∞, d and η

T°C	ε_0	n^2_D	ε_∞	$d_{gm\ cc}$	$\eta_{c.p.}$
		ethyl 3 chloropropionate.			
30	10.19	2.02	2.56	1.09	1.21
50	9 45	1 99	2.52	1.07	.91
70	8.64	1.97	2.60	1.04	.74
		methyl 3 promopropionate			
30	5 81	2.11	2 72	1.6	1.49
50	5.92	2.08	2.68	1.48	.99
70	6.10	2.06	2.50	1.45	.82
		methyl 4 chlorobrutyrate			
30	9.51	2.04	2.88	1.11	.89
50	9.12	2.01	2.56	1.08	.70
70	8.51	1 99	2.44	1.07	.55

Table 3. Values of α, τ_1, τ_2, C_1, $\Delta H\tau_1$, $\Delta H\tau_2$, $\Delta H\eta$ and μ

T°C	α	$\tau_1 \times 10^{12}$Sec.	$\tau_2 \times 10^{12}$Sec..	C_1	$\Delta H\tau_1$	$\Delta H\tau_2$	$\Delta H\eta$	μ (Debye)
			Ethyl 3 chloropropionate.					
30	.22	34.6	5.1	.71	1 87	2.68	2.65	2.27
50	.18	25.5	4.4	.72	—	—	—	2.88
70	.18	21.1	3.3	.73	—	—	—	2.23
			methyl 3 brompropionate.					
30	.20	48.2	6.8	.72	0.9	1.11	3.11	2.15
50	.21	40.7	5.9	.70	—	—	—	2.17
70	.24	36.0	4.8	.65	—	—	—	2.26
			methyl 4 chlorobutyrate					
30	.24	31.3	3.8	.67	1.13	1 74	2.44	2.17
50	.29	27.7	2.9	.65	—	—	—	2.20
70	.29	22.4	2.4	.59	—	—	—	2.25

4. Discussion

It can be seen from Table 3 that the reduced molecular relaxation time (τ_1/η) in the three esters, ethyl 3 chloropropionate, methyl 3 bromopropionate and methyl 4 chlorobutyrate at 30°C are 28.6, 32.0 and 35 p.Sec. respectively and are consistent with the increasing sizes of the molecules.

The values of these relaxation times compare well with the molecular relaxation time $\tau_1 \approx 34$ p.sec. at 30°C in ethylchloroacetate reported by Srivastava and Dinanath (1973). The shorter relaxation time τ_2 lying in the range

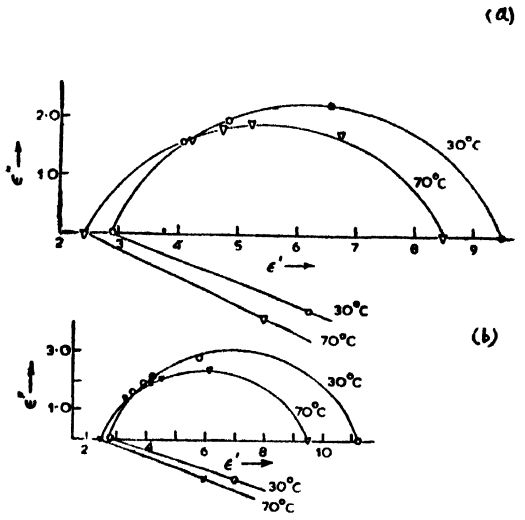


Fig. 1. Cole Cole plots of (a) me- 4 chl. butyrate (b) ethyl-3 chl propionate

4-5 ps at 30°C in the present esters compares well with the CH_2Cl group rotation (4.4 p.s) in benzylchloride in the liquid state (Turner et al 1970) and is therefore attributed to the relaxation time of CH_2Cl group rotation in ethyl 3 chloropropionate and methyl 4-chlorobutyrate. Similarly the shorter relaxation time τ_2 of 6.8 p.sec. at 30°C in methyl 3 bromopropionate which comparable to the of CH_2 Br group rotation (6.3 p.Sec.) in benzyl bromide (Hasan *et al* 1971), is evidently due to the rotation of CH_2 Br group in the methyl bromopropionate. It may be noted here that both molecular and group relaxation times decrease with increase of temperature, though the rate of their decrease is quite different.

Weight factors : As can be seen from table 3, that the value of weight factor $C_1 \approx .65—.7$ in all the esters, indicating that molecular reorientation is the major relaxation process in all of them. This value of C_1 is in conformity with the value of $C_1 \approx .65$ in halobutyrates reported by Srivastava and Dinanath (1974).

Distribution Parameter : The value of the distribution parameter (table 2) in found to be appreciably large in all the esters and it is the highest in the methyl 4-chlorobutyrate. This indicates that the number of relaxation processes in the methyl 4-chlorobutyrate is larger than the other two esters.

It is quite plausible because there are two axes of internal rotation in the propionates, while, in the chlorobutyrates there are three such rotational axes.

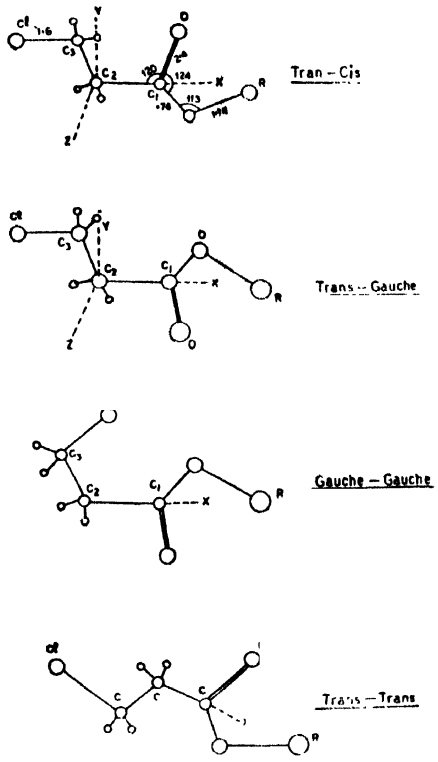


Fig. 2a. Conformers of methyl 3 bromopropionate

Potential barriers to molecular and internal rotation : The barrier to molecular reorienntation $\Delta H\tau_1$ (Table 3) in the case of ethyl-3 chloropropionate is highest ($\Delta H\tau_1 \approx 1.87$ kcal/mole) and is lowest in methyl 3-bromopropionate ($\Delta H\tau_1 \approx 1$ kcal/mole). The barrier to internal rotation ($\Delta H\tau_2$) in each case is found to be higher than the corresponding value for the barrier to molecular reorientation.

Dipole moment and molecular configurations : The experimentally obtained values of the dipole moment is found to lie in the range 2.2-2.3D (table 3) in all the three esters and is almost temperature independent. The existence of the internal rotation in each of the esters, as discussed above, suggests that the possibility of several rotamers in each esters having two/three axes of internal rotation. Assuming there are a few forms (Fig 2) trans-cis, trans-gauche and trans-trans, (Fig. 2a) present in the ethyl 3-chloropropionate

and methyl 3-bromopropionate, the dipole moment of each form was caluculated from the bond moments and bond angles by vector addition. The values of the calculated moment for TC, TG and TT are about 1.9D and is nearly

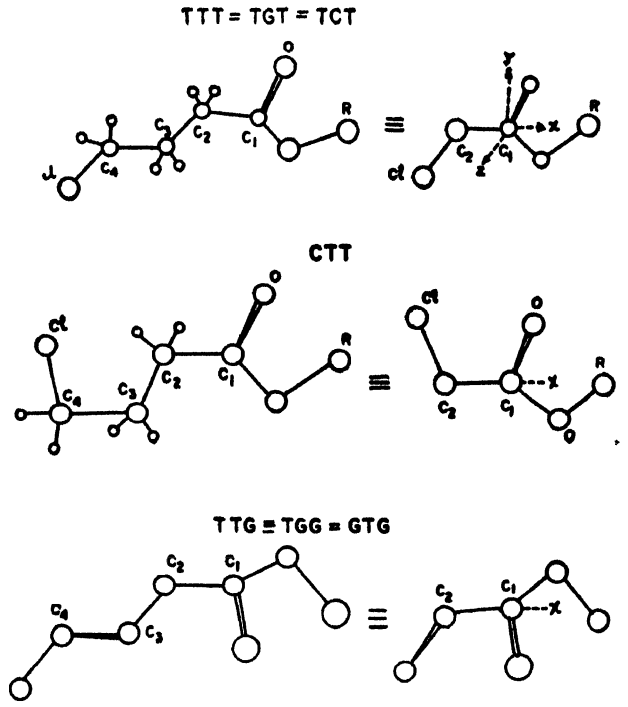


Fig. 2b. Conformes of methyl 4 chlorobutyrate

equal to the observed dipole moment. The calculated moment for the GG form is about 3.24D which is much larger than the observed value of 2.2D. So it is concluded that the esters of ethyl 3 chloropropionate and methyl 3 bromopropionate consist of TC, TG and TT forms, which having similar moments, the apparent moment does not change with temperature. It may be noted here that Som *et al* (1976) reported the presence of at least two forms of rotamers in these esters of which TC is more stable than the other. The ester of methyl 4-chlorobutyrate has three internal axes of rotation and has about eight possible rotamers of which TTC, TTG, TGG, TGT and TTT (Fig 2b) are considered for calculation.

The observed moment of 2.2D agrees well with the calculated moment of 2.4D for TTG and TGG forms, but differ much from that of TTC (3.2D) and TGT & TTT ($\mu \approx$ .3D). It is therefore concluded that the major constituents of methyl 4-chlorobutyrate are TTG and TGG conformers.

ACKNOWLEDGMENT

We thank Prof. G. S. Kastha for his kind interest.

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